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Synthesis and Mössbauer study of anomalous magnetic behavior of Fe_2O_3 nanoparticle-montmorillonite nanocomposites

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Abstract

In ensembles of single-domain magnetic nanoparticles, a magnetic-dipole interaction between particles takes place. The controlled assembly of bulk magnetically ordered materials from such nanoparticles opens up wide prospects for the creation of new magnetic materials. One of the classical methods for obtaining an ordered ensemble of nanoparticles is their synthesis in a matrix of clay minerals such as montmorillonite. The interlayer space of the mineral acts as a nanoreactor with specific conditions for the particle synthesis. Intercalating iron polycations into montmorillonite, one can obtain well-ordered ensembles of magnetic nanoparticles. Magnetic nanocomposites created in this way have new properties and exhibit non-standard magnetic behavior, which cannot always be described in terms of classical concepts. We used the capabilities of Mössbauer relaxation spectroscopy to study magnetic nanocomposites in order to study the structural and magnetic features of nanoparticles formed in aluminosilicate layers "from the inside". An analysis of the Mössbauer spectra revealed that ordered ensembles of antiferromagnetic α-Fe_2O_3 nanoparticles formed between aluminosilicate layers of montmorillonite exhibited ferromagnetic behavior.

Keywords Mössbauer spectroscopy · Magnetic nanoparticles · Intercalation · Montmorillonite · Antiferromagnetic nanoparticles

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1 Introduction

Due to its unique properties, magnetic single-domain nanoparticles are of great interest for research from a wide range of scientific fields, such as chemical catalysis, biotechnology and biomedicine, data storage, ecology, etc. [1–5]. Superparamagnetic behavior at room temperature is characteristic of iron oxide nanoparticles whose size is below a critical value (usually 10–20 nm). The ensembles of such nanoparticles are characterized by a magnetic dipole interaction between particles, which can be compared the exchange interaction. In such a system of single-domain magnetic particles, a dipole magnetic order develops. The controlled assembly of large magnetically ordered structures from such nanoparticles opens up prospects for the creation of completely new magnetic materials [6–8]. For the targeted synthesis of a dipole-bound magnetic metamaterial, an understanding of the fundamental relationships between the structural coordination of nanoparticles in an ensemble and the magnetic ordering arising in such a structure is necessary. The most important here is a direct study and the subsequent description of the magnetic dynamics of an ensemble of single-domain nanoparticles in a fabricated nanocomposite material.

One of the traditional methods for obtaining an ordered ensemble of nanoparticles with known structural characteristics is their direct synthesis in the interlayer space of layered aluminosilicates, such as montmorillonite [9, 10]. Montmorillonite is a clay mineral, consisting of stacked on top of each other packets of aluminosilicate plates with a thickness of the order of 1 nm, separated by an interlayer space. Due to its surface-active properties, this mineral is widely used for modification with polymers and organic compounds [11, 12]. By intercalating the solution, a cation exchange can be carried out, as a result of which simple interlayer cations (usually Na^+) are replaced by cations from the solution. Intercalation and subsequent stable incorporation of inorganic compounds into the interlayer space allows one to obtain a clay hybrid material with a characteristic “pillar” structure. A wide range of ordered pillar structure metamaterials based on metal nanoparticles and their oxides were obtained by intercalation of montmorillonite with polycations of various metals [13–16].

By intercalating the iron polycations into montmorillonite, it is possible to obtain a pillar structure, which is formed by small magnetic nanoparticles arranged between aluminosilicate packets. The resulting magnetic nanocomposites possess new properties and exhibit non-standard magnetic behavior [17, 18]. It was shown that the specific magnetization of nanoparticles encapsulated in a montmorillonite matrix can be almost two orders of magnitude higher than the specific magnetization of free hematite nanoparticles [19]. On the other hand, in a number of studies, suppression of the magnetic properties of intercalated nanoparticles was observed in samples of aluminosilicate magnetic nanocomposites [18]. In general, all works in this field indicate the non-standard behavior of magnetic clay nanocomposites, which often cannot be explained in terms of classical concepts.

In this work, we investigated the samples of montmorillonite intercalated with iron polycations using Mössbauer relaxation spectroscopy to study the structural and magnetic features of nanoparticles formed in aluminosilicate layers. The method of synthesis of polycations and intercalation conditions critically affect the properties of the manufactured nanocomposite. We used polycations prepared under various conditions to obtain two different samples. To study the formation of particles in the interlayer space of clay, obtained nanocomposites were investigated before and after calcination. Structural features and magnetic behavior of nanoparticles formed in montmorillonite were analyzed based on the parameters of the Mössbauer spectra measured at different temperature points.

2 Experiment

2.1 Chemicals

As the starting reagent of montmorillonite MMT-Na+, specially prepared cloisite (Cloisite-Na+, BYK) was used. For the preparation of iron polycations, iron (III) chloride (Sigma Aldrich, reagent grade 97%) and sodium hydroxide (Sigma Aldrich, reagent grade $\geq$ 97%) were used.

2.2 Synthesis of iron polycations

Polycations were prepared in a chemical reaction by adding an aqueous solution of 1.6 g of NaOH in 3.25 g of $FeCl_3$ dissolved in 100 ml of deionized water at 70 °C. The obtained polycations were aged under vigorous stirring for 2 h at 70 °C. A second sample of iron polycations at a reaction and aging temperature of 30 °C was prepared in the same way.

2.3 Magnetic clay nanocomposite manufacturing

To prepare a 1% (wt) aqueous dispersion of montmorillonite, 1 g of the clay powder MMT-Na + was dissolved in 100 ml of deionized water with stirring until a homogeneous solution was obtained. Then, the solution of iron polycations (0.01 mol Fe per 1 g of clay) was added to the dispersion with vigorous stirring at room temperature. The resulting solution was stirred for one hour. Modified clay samples were precipitated using a centrifuge (6000 rpm, 10 min), the supernatant was removed, after which the samples were diluted with 30 ml of deionized water. Washing of the samples was repeated 10 times and then they were dried at 80 °C for 24 h. Half of each sample was collected in a crucible and annealed at a temperature of 550 °C for 2 h in an air atmosphere. In accordance with the temperature at which the intercalating iron polycations were synthesized, the samples of the hybrid material were named MMT30 and MMT70.

2.4 Mössbauer spectroscopy

^{57}Fe Mössbauer spectra were measured at different temperatures with electro-dynamical type spectrometer CMS-1104Em, working in the constant acceleration mode. ^{57}Co in a rhodium matrix was used as a source of the resonant gamma-irradiation. Isomer shifts were determined in relation to α-Fe.

2.5 Magnetization measurements

Magnetization curves M(H) were measured using a vibrating sample magnetometer (VSM) 7400 (Lake Shore Cryotronics). Experiments were carried out in magnetic field up to 5 kOe at room temperature (297 K).

3 Results

In this work, the Mössbauer spectra of two montmorillonite samples were studied after the ion exchange reaction with iron polycations. Dehydrated samples were studied before calcination, when the nanocomposite structure was made of the initial polycations, and after calcination, when all the iron of the pillared structure converted to the oxide phase.

Regardless of the temperature of iron polycations synthesis, both samples of non-calcined clay nanocomposites exhibit a single narrow doublet at 78 K and 297 K (Fig. 1 above, Fig. 2 above). The parameters of the isomeric shift and quadrupole splitting of doublets (Table 1) are in good agreement with the parameters of the spectra of polycations successfully intercalated into montmorillonite before calcination, which were obtained in [20]. The decomposition of iron chloride in sodium hydroxide is accompanied by the formation of a gel, in which iron polycations form near-spherical particles with a diameter of 15–40 Å [21]. Such particles do not have a definite phase composition and regular crystalline structure and consist mainly of oxyhydroxide forms of iron [22]. The absence of magnetic hyperfine splitting in the obtained spectra confirms the assumption that aluminosilicate packets were successfully modified with iron polycations before annealing, but magnetic nanoparticles in the interlayer space have not yet been formed.

Annealing at 550° C led to a significant change in the shape of the spectral lines of the MMT30 and MMT70 samples. A transformation of the narrow doublet in the spectra measured at room temperature into a superposition of the doublet and the significantly broadened hyperfine structure in the spectra measured at liquid nitrogen temperature is observed. The spectrum of the MMT70 has a more intense contribution from the hyperfine structure, which indicates a larger average particle size compared to the MMT30.

According to the work [17] calcination of layered aluminosilicates with intercalated iron polycations at temperatures above 500 °C leads to the formation of a pillar structure in the interlayer space formed by antiferromagnetic α-Fe_2O_3 nanoparticles.

However, the spectral line shape for both of the samples differs significantly from the typical spectrum of the bulk hematite. Over the entire temperature range, the absorption spectrum of antiferromagnetic particles is a superposition of well-resolved magnetic hyperfine structure and a single line (or a quadrupole doublet) [23]. The spectral lines of nanoparticles with an uncompensated magnetic moment are explained by the characteristic spectrum of their

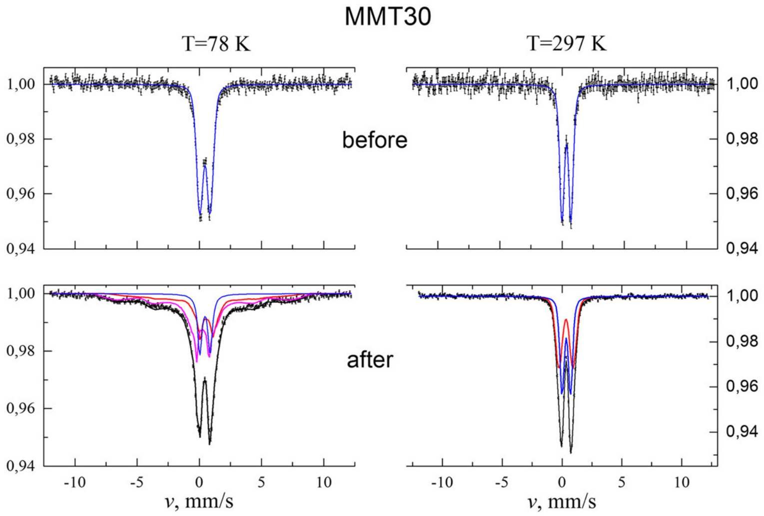

Fig. 1 ^{57}Fe Mössbauer spectra of superparamagnetic iron MMT30 nanoparticles, intercalated in Na^+ montmorillonite, measured at 297 K and 78 K

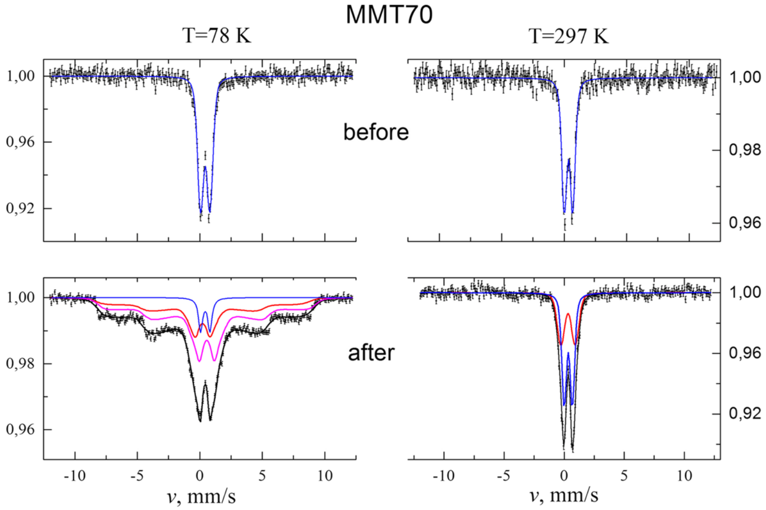

Fig. 2 ^{57}Fe Mössbauer spectra of superparamagnetic iron MMT70 nanoparticles, intercalated in Na^{+} montmorillonite, measured at 297 K and 78 K

excitations [24, 25] (see Fig. 3). A preliminary analysis of the spectra of the calcined samples revealed the presence of two independent components of the hyperfine structure, which is direct evidence of the presence of two nonequivalent crystalline sublattices. On the other hand, the Mössbauer spectrum of the regular hematite below or above Morin transition temperature should consist of only one sextet component. However, there are several reports on the non-observation of Morin transition in hematite nanoparticles with size less than 20 nm [26–28]. Thus, the samples have a ferrimagnetic structure. In addition, the relative intensity of the central doublet in the low-temperature spectra is significantly lower than in the model spectra of antiferromagnetic particles [23] (Fig. 3). It can be concluded that the spectra of calcined MMT30 and MMT70 samples that we obtained cannot be described in the framework of the generalized theory of the magnetic dynamics of antiferromagnetic nanoparticles.

Taking into account the consideration above, the spectra of both calcined samples were by a superposition of the quadrupolar doublet of lines characteristic of non-annealed samples and a magnetic hyperfine structure calculated within the model of two ferrimagnetic sublattices according to the procedure proposed in [25]. The corresponding parameters are shown in Tables 1 and 2. The values of hyperfine fields for both sublattices values are presented in the absence of temperature excitations, i.e. at T = 0 K [24]. For a rough estimation of the particle

Table 1 Spectral Mössbauer parameters of doublet components for MMT30 and MMT70 samples. Doublets with these parameters are present in the spectra of the corresponding samples both before and after their calcination; δ-isomer shift; Δ-quadruple splitting

Doublet components

Sample	T	δ, mm/s	Δ, mm/s
MMT30	78 K	0.460(3)	0.832(6)
	297 K	0.357(4)	0.721(7)
MMT70	78 K	0.439(5)	0.745(7)
	297 K	0.348(6)	0.669(9)

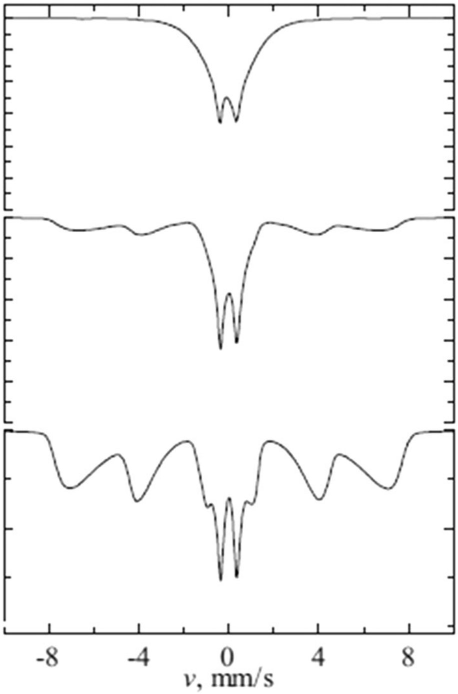

Fig. 3 Calculated ^{57}Fe Mössbauer absorption spectra of an ensemble of slowly relaxing ideal antiferromagnetic particles calculated in [24] for different values of the effective energy barrier kV/k_BT 0.1, 1.0 and 2.0 respectively in the presence of the quadrupolar hyperfine interaction with the constant q = 0.35 mm/s

size, we can make an assumption about their spherical shape. We can also take the value of the anisotropy constant equal to the constant for the hematite sample $K = 2.95 \cdot 10^3$ J/m3 from [29]. Such an approximation gives the sizes of the pillarizing particles of 1.9 and 3.5 nm for samples MMT30 and MMT 70, respectively. These values significantly exceed the thickness of the interlayer space of the initial Na^+ montmorillonite.

The results of magnetic measurements of MMT30 and MMT70 samples after calcination are presented in Fig. 4. The magnetization curve of the MMT30 demonstrates paramagnetic behavior. The MMT70 sample demonstrates superparamagnetic behavior. The absence of

Table 2 Spectral Mössbauer parameters of sextet components for MMT30 and MMT70 samples after calcination; i-number of component; H_{hf}-hyperfine field; KV-energy of magnetic anisotropy; ΔD/D - relative size distribution

Sextet components

Sample	T	i	δ, mm/s	Δ, mm/s	H_{hf}, kOe	KV/k_B, K	ΔD/D
MMT30	778 K	1	0.304(3)	0.96(2)	484(5)	0.78(8)	0.53(2)
		2	0.61(5)	0	543(3)		
	297 K	1	0.35(1)	0.71(5)	0		
		2	0.328(5)	1.18(1)	0		
MMT70	78 K	1	0.23(3)	1.12(2)	540(10)	4.8(8)	0.54(2)
		2	0.56(1)	0	551(5)		
	297 K	1	0.342(7)	0.68(2)			
		2	0.32(1)	1.2(4)			

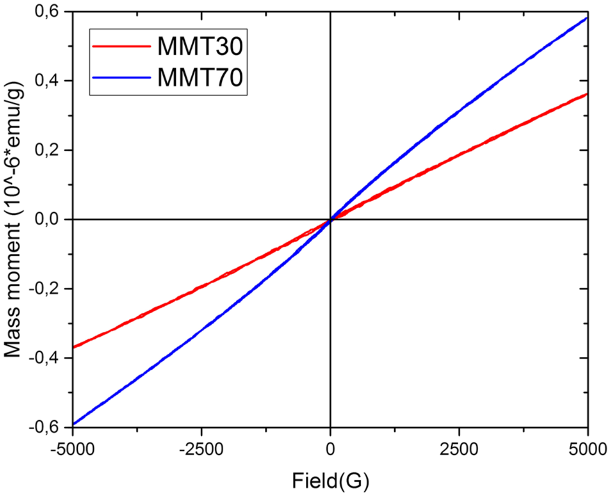

Fig. 4 Magnetization curves of MMT30 (red) and MMT70 (blue) samples at room temperature

hysteresis loops in both sample curves corresponds to the low anisotropy energy (see Table 2) and a small size of superparamagnetic particles [27].

4 Discussion

An antiferromagnetic material is characterized by the presence in its structure of two crystalline sublattices, the magnetization vectors of which fully compensate each other's magnetic contributions. Sol-gel synthesis can be considered as one of the traditional methods for producing antiferromagnetic α-Fe_2O_3 nanoparticles [30].

High-temperature annealing of the gel in an air atmosphere, obtained by decomposition of iron (III) salts excludes the possibility of the presence of the oxychloride residues component in the spectra of calcined samples, since irreversible oxidation of iron oxychloride to the iron oxide phase occurs at 400 °C [31]. The presence of an intermediate maghemite iron oxide phase is also excluded, since ferrimagnetic maghemite nanoparticles are transformed into antiferromagnetic hematite nanoparticles at an annealing temperature above 380 °C in an oxygen atmosphere [32].

In our work, the synthesis of nanoparticles in the samples MMT30 and MMT70 was carried out using standard chemical reactions for obtaining hematite particles by sol-gel method. However, the direct formation of particles took place under the specific conditions of the interlayer space of the aluminosilicate mineral. As the result, an uncompensated magnetic moment in nanoparticles appeared, which was clearly demonstrated by the Mössbauer spectra: calcined samples exhibit ferrimagnetic behavior. This effect is observed regardless of the conditions for the synthesis of intercalated iron polycations. Ferrimagnetism of nanoparticles in our nanocomposites, which is not typical for iron oxide nanoparticles calcined at temperatures above 500 °C, may be caused by the geometric features of the nanoreactor. Due to the limited interpackage space during the particles formation, an additional anisotropy axis appears which could prevent the formation of equivalent crystal hematite sublattices.

The synthesized magnetic clay nanocomposites are an extremely interesting material that demonstrates non-standard magnetic behavior. As part of further research, it is planned to perform synchrotron measurements of the structure and more detailed Mössbauer studies using isotopically enriched precursors.

5 Conclusion

Experimental data demonstrated the anomalous magnetic behavior of nanoparticles in clay nanocomposites. An analysis of the Mössbauer spectra shows that Fe_2O_3 nanoparticles formed by intercalation of iron polycations and calcination at 550 °C between aluminosilicate packages of montmorillonite exhibit ferrimagnetic behavior.

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